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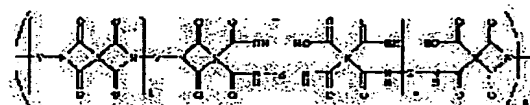
(72)Inventor : TOKUHISA KIWAMU  
TOKUMITSU AKIRA  
TAKARABE SATOSHI

## (54) RESIN SOLUTION COMPOSITION FOR ELECTRONIC MATERIAL

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a resin solution composition which is excellent in storage stability and capable of being cured at relatively low temperature and can give a cured product having an excellent balance among properties such as heat resistance, high-frequency characteristics, chemical resistance and stress relaxation properties.

**SOLUTION:** This composition is prepared by dissolving 100 pts.wt. siloxane polyimide-amic acid copolymer resin comprising an imide part prepared by the polycondensation reaction of an aromatic tetracarboxylic dianhydride with a siloxanediamine and an amic acid part prepared by the polyaddition reaction of an aromatic tetracarboxylic dianhydride with an aromatic diamine component other than the siloxanediamine and represented by the formula (wherein X is a residue of an aromatic tetracarboxylic dianhydride, Y is a residue of a siloxanediamine; Z is a residue of an aromatic diamine; (l) and (m) are each an integer; and (n) is a number of 1 or greater).



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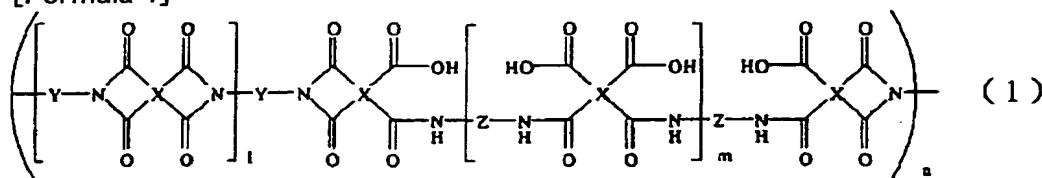
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## CLAIMS

## [Claim(s)]

[Claim 1] The resin solution constituent for electronic ingredients which comes to dissolve the siloxane polyimide amic acid copolymerization resin 100 weight section, and the epoxy resin 1 - 50 weight sections expressed with the following general formula (1) which has the amic acid part which comes to carry out the polyaddition of the aromatic series diamine components other than siloxane diamine to the imide part and aromatic series tetracarboxylic dianhydride which come to carry out the polycondensation of the siloxane diamine to aromatic series tetracarboxylic dianhydride in an organic solvent.

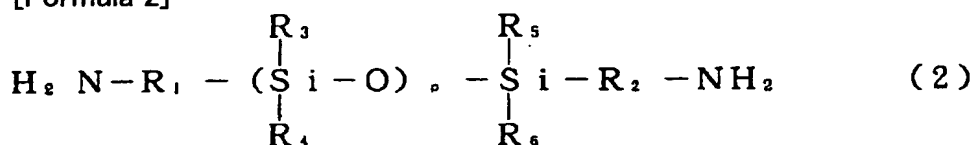
## [Formula 1]



(the inside of a formula, and X — aromatic series tetracarboxylic dianhydride residue — Y — siloxane diamine residue — in Z, l and m show an integer and n shows one or more numbers for aromatic series diamine residue independently, respectively)

[Claim 2] The resin solution constituent for electronic ingredients according to claim 1 whose mole ratios of siloxane diamine and aromatic series diamine siloxane diamine is expressed with the following general formula (2), and are 30 / 70 - 99/1.

## [Formula 2]



(Among a formula, in R1 and R2, R3 -R6 shows the hydrocarbon group of carbon numbers 1-6, and p shows the integer of 1-30 for the hydrocarbon group of bivalence, respectively)

[Claim 3] The resin solution constituent for electronic ingredients according to claim 2 whose mole ratios of siloxane diamine and aromatic series diamine the average repeat units (p) of siloxane diamine expressed with a general formula (2) are 1-12, and are 50 / 50 - 99/1.

[Claim 4] the logarithm of siloxane polyimide amic acid copolymerization resin — the resin solution constituent for electronic ingredients according to claim 1 to 3 whose viscosity is 0.08-1.2.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin solution constituent for electronic ingredients available in the interlayer insulation film of wiring components, such as a printed circuit board, a surface protective coat or the die bonding agent for semiconductor packages, liquefied encapsulant, the other heat-resistant adhesives for electronic ingredients, etc.

[0002]

[Description of the Prior Art] Using an aromatic polyimide varnish or an aromatic polyimide precursor (aromatic series polyamic acid) varnish as protective coats (interlayer insulation film etc.) of electric insulation is already variously proposed in JP,62-242393,A etc. In this case, since aromatic polyimide does not dissolve in almost all organic solvents, the polyamic acid varnish which is the precursor of the polyimide which was comparatively excellent in solvent fusibility is used in many cases. However, since hardening processing of long duration was needed at an elevated temperature 250 degrees C or more in order to complete a final imide-ized reaction after applying to a substrate etc. and removing a solvent, the aromatic series polyamic acid varnish had a problem from the point of a hardening facility, workability, and productivity. Moreover, when a polyamic acid varnish was used for protective coats, such as a printed circuit board, the oxide film arose on the copper foil circuit front face by heat treatment in an elevated temperature, and it had also become the cause of reducing dependability.

[0003] on the other hand, the chemical structures, such as the ether, a sulfone, and a ketone, be introduced into the principal chain, and also in the aromatic series polyamic acid varnish which improved solvent solubility, only the thing of about about twenty% of resin concentration could also use the highest from the limit in a spreading property etc., but the resin concentration in an organic solvent had the problem that sufficient thickness be once obtained by processing, when thick film spreading be a required application.

[0004] Although the polyimide and polyamic acid which introduced siloxane diamine into the polymer principal chain by copolymerization were proposed as technique for solving the problem of this curing temperature and solvent fusibility (JP,57-143328,A, JP,58-13631,A) and the improvement of curing temperature and solvent fusibility was achieved according to the copolymerization ratio of siloxane diamine, the problem that solvent resistance fell conversely arose.

[0005] Especially the siloxane polyimide resin with a high siloxane diamine copolymerization ratio is N,N-dimethylacetamide and the N-methyl -2. - It had the fault that the solvent resistance over general-purpose ketone solvent, such as an acetone and a methyl ethyl ketone, was low, and an application was limited, not to mention glyme system solvents, such as amide series solvents, such as a pyrrolidone, and a jig lime.

[0006] Furthermore, it was easy to hydrolyze according to moisture absorption of the moisture to the inside of a varnish easily, and the polyamic acid varnish using the general-purpose siloxane diamine which has amino alkyl structure at the end had the trouble that viscosity fell during preservation.

[0007]

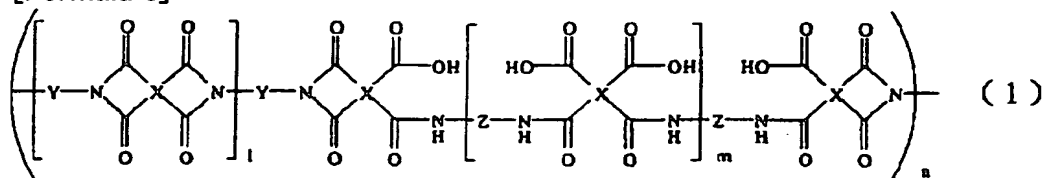
[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the resin solution constituent for electronic ingredients which gives the hardened material which was excellent in preservation stability, and cold cure was comparatively possible for and was excellent in the balance of the thermal resistance after hardening, a high frequency property, chemical resistance, a stress relaxation characteristic, etc.

[0008]

[Means for Solving the Problem] As a result of this invention persons' repeating examination wholeheartedly about this technical problem, the resin solution constituent which comes to dissolve at homogeneity the polyimide amic acid copolymerization resin which has the amic acid part which consists of the imide part and aromatic series tetracarboxylic dianhydride which consist of aromatic series tetracarboxylic dianhydride and siloxane diamine, and aromatic series diamine, and an epoxy resin in an organic solvent came to complete a header and this invention for the ability of said technical problem to be attained.

[0009] That is, this invention is a resin solution constituent for electronic ingredients which comes to dissolve the siloxane polyimide amic acid copolymerization resin 100 weight section, and the epoxy resin 1 - 50 weight sections expressed with the following general formula (1) which has the amic acid part which comes to carry out the polyaddition of the aromatic series diamine components other than siloxane diamine to the imide part and aromatic series tetracarboxylic dianhydride which come to carry out the polycondensation of the siloxane diamine to aromatic series tetracarboxylic dianhydride in an organic solvent.

[Formula 3]



(the inside of a formula, and X — aromatic series tetracarboxylic dianhydride residue — Y — siloxane diamine residue — in Z, l and m show an integer and n shows one or more numbers for aromatic series diamine residue independently, respectively)

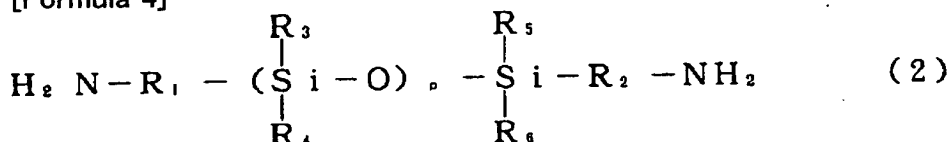
[0010] Hereafter, this invention is explained to a detail. The aromatic series tetracarboxylic dianhydride used in this invention means the compound which the carboxylic-acid radical combined with aromatic series. When the example of aromatic series tetracarboxylic dianhydride is given, pyromellitic acid 2 anhydride, — benzophenone tetracarboxylic dianhydride, 2, 2', and 3, 3', 4, and 4' 3, 3'-benzophenone tetracarboxylic dianhydride, 2, 3, 3', 4'-benzophenone tetracarboxylic dianhydride, naphthalene — 2, 3, 6, 7 — Tetracarboxylic dianhydride, Naphthalene — 1, 2, 5, 6 — Tetracarboxylic dianhydride, naphthalene — 1, 2, 4, 5 — Tetracarboxylic dianhydride, Naphthalene — 1, 4, 5, 8 — Tetracarboxylic dianhydride, naphthalene — 1, 2, 6, 7 — Tetracarboxylic dianhydride, 2, 6-dichloro naphthalene — 1, 4, 5, 8 — Tetracarboxylic dianhydride, 2, 7-dichloro naphthalene — 1, 4, 5, 8 — Tetracarboxylic dianhydride, 2, 3, 6, 7-tetrachloronaphthalene — 1, 4, 5, 8 — Tetracarboxylic dianhydride, 1, 4, 5, 8-tetrachloronaphthalene — 2, 3, 6, 7 — Tetracarboxylic dianhydride, — diphenyl tetracarboxylic dianhydride, 2, 2', and 3, 3', 4, and 4' 3, 3'-diphenyl tetracarboxylic dianhydride, 2, 3, 3', 4'-diphenyl tetracarboxylic dianhydride, 3, and 3'', 4, 4''-para terphenyl tetracarboxylic dianhydride, 2 and 2'', 3, 3''-para terphenyl tetracarboxylic dianhydride, 2, 3, and 3'', 4''-para terphenyl tetracarboxylic dianhydride, 2 and 2-bis(2 3 - dicarboxy phenyl)-propane 2 anhydride, 2 and 2-bis(3 4 - dicarboxy phenyl)-propane 2 anhydride, Screw (2 3 - dicarboxy phenyl) Ether 2 anhydride and screw (2 3 - dicarboxy phenyl) Methane 2 anhydride, Screw (3 4 - dicarboxy phenyl) Methane 2 anhydride and screw (2 3 - dicarboxy phenyl) Sulfone 2 anhydride, Screw (3 4 - dicarboxy phenyl) Sulfone 2 anhydride, 1, and 1-screw (2 3 - dicarboxy phenyl) Ethane 2 anhydride, 1 and 1-screw (3 4 - dicarboxy phenyl) Ethane 2 anhydride, Perylene — 2, 3, 8, 9 — Tetracarboxylic dianhydride, perylene — 3, 4, 9, 10-tetracarboxylic dianhydride, Perylene — 4, 5, 10, 11 — Tetracarboxylic dianhydride, perylene — 5, 6, 11, 12 — Tetracarboxylic dianhydride, Phenanthrene — 1, 2, 7, 8 — Tetracarboxylic dianhydride,

phenanthrene - 1, 2, 6, 7 - Tetracarboxylic dianhydride, Phenanthrene - 1, 2, 9, 10-tetracarboxylic dianhydride, pyrazine - 2, 3, 5, 6 - Tetracarboxylic dianhydride, thiophene - 2, 3, 4, 5 - Tetracarboxylic dianhydride, 4, 4' - Oxy-JIFUTARU acid 2 anhydride etc. is mentioned. These may be used independently and may use two or more sorts together. It is especially a screw (3,4 - dicarboxy phenyl) among these. Since sulfone 2 anhydride is excellent in the solubility over the organic solvent of said siloxane polyimide amic acid copolymerization resin, and adhesion with a copper surface, it is suitable.

[0011] Moreover, in this invention, aromatic series diamine is used for the diamine component used with aromatic series tetracarboxylic dianhydride for making it form the amic acid part in polyimide amic acid copolymerization resin using siloxane diamine for making it form the imide part in siloxane polyimide amic acid copolymerization resin.

[0012] As for the siloxane diamine used in this invention, it is desirable that it is what is expressed with the following general formula (2).

[Formula 4]



(Among a formula, in R1 and R2, R3 -R6 shows the hydrocarbon group of carbon numbers 1-6, and p shows the integer of 1-30 for the hydrocarbon group of bivalence, respectively)

[0013] It sets to the above-mentioned general formula (2), and is R1. And R2 It is two or more methylene groups of carbon numbers 3-5 or a phenylene group, and R3 -R6, respectively. As for a methyl group, an ethyl group, a propyl group or a phenyl group, and an average repeat unit (p), it is desirable that it is the integer of 1-20.

[0014] As a concrete compound of siloxane diamine, it is an omega and omega'-screw (2-aminoethyl), for example. Poly dimethylsiloxane, omega, and omega'-screw (3-aminopropyl) Poly dimethylsiloxane, omega, and omega'-screw (4-aminophenyl) Poly dimethylsiloxane, omega, and omega'-screw (3-aminopropyl) Poly diphenyl siloxane, omega, and omega'-screw (3-aminopropyl) A poly methylphenyl siloxane etc. is mentioned.

[0015] As for the imide part in which the aromatic series tetracarboxylic dianhydride and siloxane diamine of siloxane polyimide amic acid copolymerization resin add, and are formed, in this invention, it is desirable to form stable imide substantially.

[0016] The aromatic series diamine used by this invention means the compound which the amino group has combined with aromatic series. When the example of aromatic series diamine is given, they are 3 and 3' - Dimethyl -4, a 4'-diamino biphenyl, 4, 6-dimethyl - m - A phenylenediamine, 2, 5-dimethyl - p - Phenylenediamine, 2, 4-diamino mesitylene, 4, 4' - Methylene - G o - Toluidine, 4, 4' - Methylene - G 2 and 6 - A xylydine, 2, 4-toluene diamine, m-phenylene - Diamine, p-phenylene - Diamine, 4, 4' - Diamino - Diphenyl propane, 3, 3' - Diamino - A diphenyl propane, 4, 4' - Diamino - Bibenzyl, 3, 3' - Diamino - Bibenzyl, 4, 4' - Diamino - Diphenylmethane, 3, 3' - Diamino - Diphenylmethane, 2, and 2-screw [4-(4-amino phenoxy) phenyl] Propane, 4, 4' - Diamino - A diphenyl sulfide, 3, 3' - Diamino - Diphenyl sulfide, 4, 4' - Diamino - Diphenylsulfone, 3, 3' - Diamino - Diphenylsulfone, 4, 4' - Diamino - Diphenyl ether, 3, 3' - Diamino - Diphenyl ether, A benzidine, 3, 3' - Diamino - A biphenyl, 3, 3' - Dimethyl -4, 4'-diamino - Biphenyl, 3, 3' - Dimethoxy - A benzidine, 4, 4' - Diamino - p - Terphenyl, 3, 3' - Diamino - p - A terphenyl, 1, 5-diamino - Naphthalene, 2, 6-diamino-naphthalene, 2, 4-diamino - Toluene, meta xylene - 2 Five - Diamine, para xylene - 2 Five - Diamine, 1, and 3-screw (3-amino phenoxy) Benzene etc. is mentioned. These may be used independently and may use two or more sorts together. It is especially 2 and 2-screw [4 among these. - (4-amino phenoxy) Phenyl] Since the propane is excellent in the solubility over the organic solvent of said siloxane polyimide amic acid copolymerization resin etc., it is suitable.

[0017] In this invention, molecular weight is controllable by adjusting the mole ratio of a monomer component like the case of the usual polycondensation system polymer. Specifically, it is desirable to use 0.8-1.2-mol diamine to one mol of all aromatic series tetracarboxylic

dianhydride. If this mole ratio is smaller than 0.8 or becomes larger than 1.2, only the thing of low molecular weight will be obtained and sufficient thermal resistance will not be obtained.

furthermore -- desirable -- one mol of aromatic series tetracarboxylic dianhydride -- receiving -- 0.95-1.05 -- it is use of the diamine of 0.98 - 1.02 mole ratio most preferably.

[0018] As for the mole ratio of siloxane diamine and aromatic series diamine, in this invention, it is desirable that it is 30 / 70 - 99/1. If this mole ratio is smaller than 30/70, the solvent fusibility of siloxane polyimide amic acid copolymerization resin and the stress relaxation characteristic of hardening resin will get worse, if 99/1 is exceeded, a reacting point with the epoxy resin of siloxane polyimide amic acid copolymerization resin will decrease, and the chemical resistance of hardening resin will fall.

[0019] the siloxane polyimide amic acid copolymerization resin used in this invention -- as the standard of the molecular weight -- a logarithm -- it is desirable that viscosity is 0.08-1.2. a logarithm -- viscosity dissolves siloxane polyimide amic acid copolymerization resin in a methyl jig lime at homogeneity, prepares the concentration of 0.5g / 100ml solution, measures the solution viscosity and the viscosity of a methyl jig lime at 30 degrees C with an Ubbelohde viscometer, and computes them by the following formula.

a logarithm -- the logarithm of viscosity =  $\ln(\text{solution viscosity} / \text{solvent viscosity}) / \text{solution concentration}$  siloxane polyimide amic acid copolymerization resin -- if viscosity is lower than 0.08, the chemical resistance of hardening resin and thermal resistance will get worse, if 1.2 is exceeded, the viscosity of a resin solution constituent will become high too much, and workability will fall.

[0020] although especially the epoxy resin blended with siloxane polyimide amic acid copolymerization resin is not what is limited in this invention -- weight per epoxy equivalent -- 100-5000 -- it is 100 to about 1000 especially -- the epoxy resin of the shape of liquefied or powder is desirable. As an example of an epoxy resin, they are bisphenol A, Bisphenol F, Bisphenol S, a fluorene bisphenol, 4, and 4'. - They are biphenol, 2, and 2'. - Phenols, such as biphenol, hydroquinone, and resorcinol, tris - (4-hydroxyphenyl) The glycidyl ether compound guided from halogenation bisphenols, such as phenols more than trivalent [ , such as ethane, a phenol novolak and o-cresol novolak, ] or tetrabromobisphenol A, and a BUROMO phenol novolak, is mentioned. These may be used independently and may use two or more sorts together. In order [ for the stability of a resin solution constituent ] to obtain the hardened material which has a stress relaxation characteristic with a low elastic modulus, the bisphenol mold epoxy resin of 2 organic-functions molds with comparatively large weight per epoxy equivalent is desirable.

[0021] The loadings of an epoxy resin require that it is 1 - 50 weight section to the siloxane polyimide polyamic acid copolymerization resin 100 weight section, and are 3 - 30 weight section preferably. If the loadings of an epoxy resin exceed 50 weight sections, the stress relaxation characteristic of hardening resin, thermal resistance, etc. will fall, and if fewer than 1 weight section, chemical resistance will get worse.

[0022] Moreover, in this invention, an epoxy resin curing agent can also be blended with everything but the above-mentioned siloxane polyimide amic acid copolymerization resin and an epoxy resin for the purpose of promotion of hardening if needed.

[0023] Although not limited, if the homogeneity dissolution of this resin constituent is possible for especially the organic solvent used in this invention, even if it may be independent and is a mixed solvent which used two or more sorts together, it will not interfere. For example, glyme system solvents, such as oxane system solvents, such as amide system solvents, such as a phenol system solvent, and a pyrrolidone system solvent, an acetamide system solvent, and dioxane, a trioxane, ketone solvent, such as a cyclohexanone, and a methyl jig lime, a methyl TORIGU lime, etc. are mentioned. Moreover, aliphatic hydrocarbon system solvents, such as aromatic hydrocarbon system solvents, such as benzene and toluene, and a hexane, Deccan, etc. can also be mixed and used in the range which can be dissolved in homogeneity if needed. The weight ratio (solid content/solvent) of solid content and a solvent is (20-80)/(80-20), and the amount of an organic solvent is /(40-70) (60-30) preferably, when the total quantity of siloxane polyimide amic acid copolymerization resin and an epoxy resin is made into the amount of solid

content. If a solvent ratio exceeds 80, it will become difficult to obtain the hardened material of sufficient thickness, if there are few solvent ratios than 20, the viscosity of a resin solution constituent will become high too much, and workability will fall.

[0024]

[Embodiment of the Invention] The resin solution constituent of this invention can be prepared by the following approaches. First, the aromatic series tetracarboxylic dianhydride of an excessive amount is made to dissolve or suspend in an organic solvent to siloxane diamine beforehand, and siloxane diamine is added gradually. After stirring mixture at the temperature near a room temperature for 2 to 3 hours, it performs a polymerization and imide-ization for 10 to 24 hours, removing condensation water at the temperature to which imide-ization may advance, and obtains the siloxane polyimide oligomer which has an acid anhydride at the end. The rate of imide-izing of siloxane polyimide oligomer (%) is measured by the infrared absorption analysis-of-a-spectrum method, and is 100 % substantially, and it is desirable that there is no amic acid part. Then, add aromatic series diamine so that an acid anhydride and all diamine components may become an abbreviation equimolecular amount after cooling a reaction mixture to near a room temperature, and it is made to react at the temperature to which imide-ization does not advance, and a siloxane polyimide polyamic acid copolymerization resin solution is obtained. Subsequently, the resin solution constituent of this invention is obtained by making homogeneity dissolve an epoxy resin in a polyimide polyamic acid copolymerization resin solution.

[0025] Although it is good by especially the organic solvent used for a reaction not being limited here, and using the aforementioned organic polar solvent, the thing more than boiling point 150 \*\* is good by the problem of compaction of reaction time, and solvent dissipation, and the organic polar solvents (for example, methyl TORIGU lime etc.) which are especially 200 \*\*s more than are the most desirable.

[0026] A hardening accelerator better known than before, a coupling agent, a bulking agent, a pigment, a thixotropy nature grant agent, a defoaming agent, etc. may be suitably blended with the resin solution constituent of this invention other than each above-mentioned component if needed.

[0027]

[Example] Hereafter, an example explains this invention to a detail. In addition, characterization of a resin solution constituent was performed by a following matter and the following evaluation approach.

[0028] 18 micrometers in [solder thermal-resistance] thickness To the copper roughening side of copper foil (0.5 by Mitsui Mining & Smelting, Inc. ounce rolling foil), the thickness after heat treatment is 15-20 micrometers. The resin solution constituent prepared to each presentation is cast so that it may become, it heat-treats for 30 minutes by 180 \*\* after predrying for 15 minutes by 130 \*\*, and a paint film is created. 1cm x2cm Solder thermal resistance was evaluated \*\*\*\*\* having been produced, having been immersed in the melting solder bath adjusted to 300 \*\* for 60 seconds, having made the thing without the exfoliation from the copper front face of a coat, or change to a coat exterior into O, and having used as x what change produced in exfoliation or a coat exterior.

[0029] 35 micrometers in [elastic-modulus] thickness To copper foil (the Mitsui Mining & Smelting, Inc. make and 1 ounce rolling foil), the thickness after heat treatment is 15-20 micrometers. The resin solution constituent prepared to each presentation is cast so that it may become, it heat-treats for 30 minutes by 180 \*\* after 15-minute predrying at 130 degrees C, and a paint film is produced. After an etching reagent removes copper completely, a 12.5cmx20cm coat test piece is produced, and it attaches in a hauling testing machine (Oriental energy machine incorporated company make, STROGRAPH-R1), and the copper foil by which paint film formation was carried out is 100kg of loads, and hauling rate 5 mm/min. The elastic modulus was measured.

[0030] [— a logarithm — the logarithm as a standard of the molecular weight of viscosity] siloxane polyimide amic acid copolymerization resin — viscosity dissolved siloxane polyimide amic acid copolymerization resin in the methyl jig lime at homogeneity, prepared the



concentration of 0.5g / 100ml solution, measured the solution viscosity and the viscosity of a methyl jig lime at 30 degrees C with the Ubbelohde viscometer, and computed them by the following formula. a logarithm  $\text{--- viscosity} = \text{---} \ln (\text{solution viscosity} / \text{solvent viscosity}) / \text{solution concentration}$  [0031] The viscosity of the resin solution constituent prepared to [solution viscosity] each presentation was measured at 25 degrees C by the Brookfield viscometer.

[0032] 35 micrometers in [acetone extractives] thickness To copper foil (the Mitsui Mining & Smelting, Inc. make and 1 ounce rolling foil), the thickness after heat treatment is 15-20 micrometers. The resin solution constituent prepared to each presentation was cast so that it might become, it heat-treated by 180 \*\* after 15-minute predrying at 130 degrees C for 30 minutes, and the paint film was produced. After the copper foil by which paint film formation was carried out removed copper completely with the etching reagent, it produced the 10cmx10cm coat, was immersed in the 25-degree C acetone solution for 30 minutes, and made the weight decrement of a coat acetone extractives.

[0033] 35 micrometers in [dielectric constant] thickness To the copper roughening side of copper foil (the Mitsui Mining & Smelting, Inc. make and 1 ounce rolling foil), the thickness after heat treatment is 40-50 micrometers. The resin solution constituent prepared to each presentation was cast so that it might become, it heat-treated by 180 \*\* after 15-minute predrying by 130 \*\* for 30 minutes, and the paint film was produced. On the produced paint film, it is the copper roughening side of the copper foil of the same above-mentioned kind Temperature 200 \*\* and pressure 40 Kgf/cm<sup>2</sup> Thermocompression bonding was carried out for 1 hour, and double-sided copper clad laminate was produced. Subsequently, according to IPC-TM650.2.5.5A specification, circuit processing of the double-sided copper clad laminate was carried out, the test piece for dielectric constant measurement was produced, it attached in the impedance analyzer, and the dielectric constant of 1Mhz was measured.

[0034] Dean-Shyurark equipped with example of manufacture 1 stirrer, and nitrogen installation tubing To the reactor of a mold, it is a screw (3 4 - dicarboxy phenyl). 39.6g (0.110 mols) of sulfone 2 anhydrides TORIGU lime 118g is inserted in, omega and omega'-bis(3-aminopropyl) poly dimethylsiloxane 71.4g (p= 8, 0.093 mol) is dropped using a dropping funnel under nitrogen-gas-atmosphere mind, and it is about 2 at a room temperature. Time amount churning was carried out. Then, this reaction solution was heated to bottom of nitrogen-gas-atmosphere mind 190 \*\*, and heating stirring was carried out for 15 hours, removing water. Subsequently, this reaction solution is cooled to a room temperature, and it is 2 and 2-screw [4. - (4-amino phenoxy) Phenyl] It is this reaction solution at a room temperature, adding propane 7.1g (0.017 mols) and agitating at a room temperature under nitrogen-gas-atmosphere mind About 5 Time amount churning was carried out and the siloxane polyimide amic acid copolymerization resin solution of the solid content concentration 51 weight section was obtained. the logarithm of the obtained siloxane polyimide amic acid copolymerization resin  $\text{--- viscosity}$  (the temperature of 30 degrees C, concentration of 0.5g / 100ml) was 0.26.

[0035] Dean-Shyurark equipped with example of manufacture 2 stirrer, and nitrogen installation tubing To the reactor of a mold, it is a screw (3 4 - dicarboxy phenyl). 39.6g (0.110 mols) of sulfone 2 anhydrides TORIGU lime 120g is inserted in and it is omega and omega'-bis(3-aminopropyl) poly dimethylsiloxane 76.3g (p = 8 or 0.099 mols) under nitrogen-gas-atmosphere mind. It is dropped using a dropping funnel and is about 2 at a room temperature. Time amount churning was carried out. Then, this reaction solution was heated under nitrogen-gas-atmosphere mind at 190 \*\*, and heating stirring was carried out for 15 hours, removing water. Subsequently, this reaction solution is cooled to a room temperature, and it is 2 and 2-screw [4. - (4-amino phenoxy) Phenyl] It is this reaction solution at a room temperature, adding propane 4.5g (0.011 mols) and agitating at a room temperature under nitrogen-gas-atmosphere mind About 5 Time amount churning was carried out and the siloxane polyimide amic acid copolymerization resin solution of the solid content concentration 51 weight section was obtained. the logarithm of the obtained siloxane polyimide amic acid copolymerization resin  $\text{--- viscosity}$  (the temperature of 30 degrees C, concentration of 0.5g / 100ml) was 0.23.

[0036] It is a screw (3 4 - dicarboxy phenyl) to example of manufacture 3 stirrer, and the reactor

equipped with nitrogen installation tubing. 39.6g (0.110 mols) of sulfone 2 anhydrides TORIGU lime 118g is inserted in and it is omega and omega'-bis(3-aminopropyl) poly dimethylsiloxane 71.4g ( $p = 8$  or 0.093 mols) under nitrogen-gas-atmosphere mind. It is dropped using a dropping funnel and is room temperature \*\*\*\* 5. Time amount churning was carried out. Subsequently, it is 2 and 2-screw [4 to this reaction solution. - (4-amino phenoxy) Phenyl] It is this reaction solution at a room temperature, adding propane 7.1g (0.017 mols) and agitating at a room temperature under nitrogen-gas-atmosphere mind About 5 Time amount churning was carried out and the siloxane polyamic acid copolymerization resin solution of the solid content concentration 50 weight section was obtained. the logarithm of the obtained siloxane polyamic acid copolymerization resin -- viscosity (the temperature of 30 degrees C, concentration of 0.5g / 100ml) was 0.27.

[0037] 1500ml of examples 100g of siloxane polyimide amic acid copolymerization resin solutions, bisphenol A which were obtained in the example 1 of manufacture to the reactor 4.1g (the Tohto Kasei Co., Ltd. make, YD-011, weight per epoxy equivalent = 476) of mold epoxy resins was inserted in, churning mixing was carried out until it became homogeneity at the room temperature, and the resin solution constituent was obtained. A preservation stability test, elastic-modulus measurement, a solder heat test, a chemical corrosion resistance test, and dielectric constant measurement were performed using this resin solution constituent. Even if it left this resin solution constituent at the room temperature for one week, it held the condition of a uniform solution, and viscosity. Moreover, even if it left it for three months in the condition 5 degrees C or less, most viscosity change was not observed.

[0038] 2500ml of examples 100g of siloxane polyimide amic acid copolymerization resin solutions, bisphenol A which were obtained in the example 1 of manufacture to the reactor 8.2g (the Tohto Kasei Co., Ltd. make, YD-014, weight per epoxy equivalent = 956) of mold epoxy resins was inserted in, churning mixing was carried out until it became homogeneity at the room temperature, and the resin solution constituent was obtained. A preservation stability test, elastic-modulus measurement, a solder heat test, a chemical corrosion resistance test, and dielectric constant measurement were performed using this resin solution constituent. Even if it left this resin solution constituent at the room temperature for one week, it held the condition of a uniform solution, and viscosity. Moreover, even if it left it for three months in the condition 5 degrees C or less, most viscosity change was not observed.

[0039] 3500ml of examples 100g of siloxane polyimide amic acid copolymerization resin solutions, bisphenol A which were obtained in the example 2 of manufacture to the reactor 4.1g (the Tohto Kasei Co., Ltd. make, YD-011, weight per epoxy equivalent = 476) of mold epoxy resins was inserted in, churning mixing was carried out until it became homogeneity at the room temperature, and the resin solution constituent was obtained. A preservation stability test, elastic-modulus measurement, a solder heat test, a chemical corrosion resistance test, and dielectric constant measurement were performed using this resin solution constituent. Even if it left this resin solution constituent at the room temperature for one week, it held the condition of a uniform solution, and viscosity. Moreover, even if it left it for three months in the condition 5 degrees C or less, most viscosity change was not observed.

[0040] Except having not used example of comparison 1 epoxy resin, it carried out like the example 1 and a preservation stability test, elastic-modulus measurement, a solder heat test, a chemical corrosion resistance test, and dielectric constant measurement were performed. Consequently, this resin solution constituent had very bad chemical resistance, and it dissolved it in the acetone nearly completely.

[0041] 2500ml of examples of a comparison 100g of siloxane polyamic acid copolymerization resin solutions, bisphenol A which were obtained in the example 3 of manufacture to the reactor 4.1g (the Tohto Kasei Co., Ltd. make, YD-011, weight per epoxy equivalent = 476) of mold epoxy resins was inserted in, churning mixing was carried out until it became homogeneity at the room temperature, and the resin solution constituent was obtained. A preservation stability test, elastic-modulus measurement, a solder heat test, a chemical corrosion resistance test, and dielectric constant measurement were performed using this resin solution constituent. When this resin solution constituent was left for one week at the room temperature, it showed the

remarkable viscosity down. Moreover, the viscosity down even with a remarkable condition 5 degrees C or less was observed.

[0042] The result of a preservation stability test, elastic-modulus measurement, a solder heat test, a chemical corrosion resistance test, and dielectric constant measurement is hung up over Table 1 at the combination presentation list of the resin solution constituent of the above-mentioned example and the example of a comparison. Here, it is [90day] after saving solution measurement of viscosity and solder thermal resistance on the day [0day] when elastic-modulus measurement, a chemical corrosion resistance test, and dielectric constant measurement manufactured the resin solution constituent in the day [0day] which manufactured the resin solution constituent, and the condition of 5 during 90 days \*\*. It measured.

[0043]

[Table 1]

		実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
組成部	共重合樹脂溶液	100	100	100	100	100
	YD-011	4.1	0	4.1	0	4.1
	YD-014	0	8.2	0	0	0
	Bren-S	0	0	0	0	0
溶液粘度 [0day] (poise)		134	272	96	110	162
溶液粘度 [90day] (poise)		141	272	100	108	40
WLF 耐熱 [0day]		○	○	○	○	○
WLF 耐熱 [90day]		○	○	○	○	×
弾性率 (kgf/cm <sup>2</sup> )		38	37	19	27	37
γ-ブチロ可溶分 (wt%)		4	5	6	溶解	3
誘電率		3.2	3.2	3.2	3.2	3.2

[0044]

[Effect of the Invention] If the resin solution constituent for electronic ingredients of this invention is excellent in preservation stability, cold cure 180 degrees C or less is possible for it and this is hardened, the hardened material excellent in thermal resistance, a RF property, chemical resistance, a stress relaxation characteristic, etc. will be obtained. Therefore, the resin solution constituent for electronic ingredients of this invention can be used suitable for the interlayer insulation film of wiring components, such as a printed circuit board, a surface protective coat or the die bonding agent for semiconductor packages, liquefied encapsulant, the

other heat-resistant adhesives for electronic ingredients, etc.

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[Translation done.]

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(71) 出願人 000006644

新日鐵化学株式会社

東京都中央区新川二丁目31番1号

(72) 発明者 徳久 極

千葉県木更津市清見台南4-12

(72) 発明者 徳光 明

千葉県木更津市祇園4-3-8

(72) 発明者 財部 諭

千葉県君津市八重原1338-1-337

(74) 代理人 弁理士 成瀬 勝夫 (外1名)

(54) 【発明の名称】 電子材料用樹脂溶液組成物

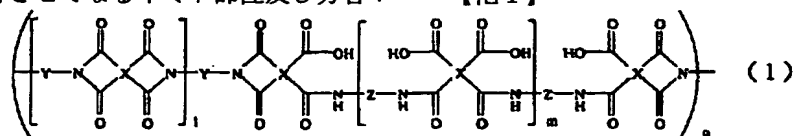
(57) 【要約】

【課題】 保存安定性に優れ、比較的低温硬化が可能で、硬化後の耐熱性、高周波特性、耐薬品性、応力緩和特性などのバランスに優れた硬化物を与える電子材料用樹脂溶液組成物を提供する。

【解決手段】 芳香族テトラカルボン酸二無水物とシロキサンジアミンを重縮合させてなるイミド部位及び芳香\*

\* 族テトラカルボン酸二無水物とシロキサンジアミン以外の芳香族ジアミン成分を重付加させてなるアミック酸部位を有する下記一般式(1)で表わされるシロキサンポリイミドアミック酸共重合樹脂100重量部とエポキシ樹脂1~50重量部とを有機溶媒に溶解してなる電子材料用樹脂溶液組成物。

【化1】



(1)

(式中、Xは芳香族テトラカルボン酸二無水物残基を、Yはシロキサンジアミン残基を、Zは芳香族ジアミン残

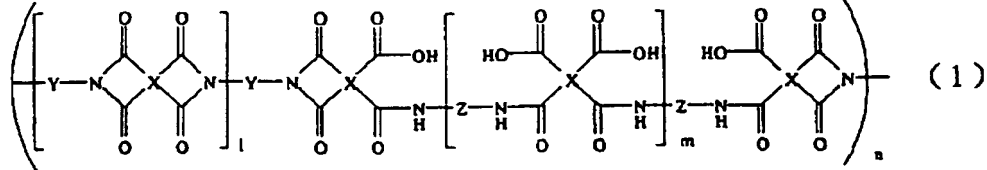
基を、l及びmはそれぞれ独立に整数を、nは1以上の数を示す)

1

2

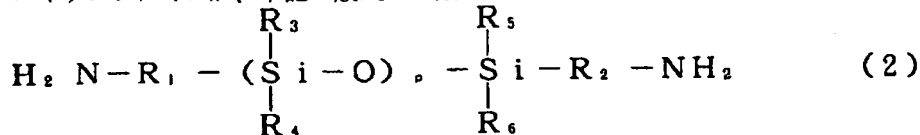
## 【特許請求の範囲】

【請求項1】 芳香族テトラカルボン酸二無水物とシロキサンジアミンを重縮合させてなるイミド部位及び芳香族テトラカルボン酸二無水物とシロキサンジアミン以外の芳香族ジアミン成分を重付加させてなるアミック酸部\*



(式中、Xは芳香族テトラカルボン酸二無水物残基を、Yはシロキサンジアミン残基を、Zは芳香族ジアミン残基を、l及びmはそれぞれ独立に整数を、nは1以上の数を示す)

【請求項2】 シロキサンジアミンが、下記一般式 ※



(式中、R<sub>1</sub>及びR<sub>2</sub>は二価の炭化水素基を、R<sub>3</sub>～R<sub>6</sub>はそれぞれ炭素数1～6の炭化水素基を、pは1～30の整数を示す)

【請求項3】 一般式(2)で表わされるシロキサンジアミンの平均繰返し単位(p)が、1～12であり、かつシロキサンジアミンと芳香族ジアミンのモル比が、50/50～99/1である請求項2記載の電子材料用樹脂溶液組成物。

【請求項4】 シロキサンポリイミドアミック酸共重合樹脂の対数粘度が、0.08～1.2である請求項1乃至3のいずれかに記載の電子材料用樹脂溶液組成物。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、プリント基板等配線部品の層間絶縁膜や表面保護膜、あるいは半導体パッケージ用ダイボンディング剤、液状封止剤、その他電子材料用耐熱接着剤などに利用可能な電子材料用樹脂溶液組成物に関するものである。

## 【0002】

【従来の技術】芳香族ポリイミドワニス又は芳香族ポリイミド前駆体(芳香族ポリアミック酸)ワニスを、電気絶縁性の保護膜(層間絶縁膜など)として利用することは、例えば特開昭62-242393号公報等において既に種々提案されている。この場合、芳香族ポリイミドは、ほとんどの有機溶媒に溶解しないため、溶剤可溶性に比較的優れたポリイミドの前駆体であるポリアミック酸ワニスを使用されることが多い。ところが、芳香族ポリアミック酸ワニスは基板などに塗布し、溶剤を除去した後、最終的なイミド化反応を完結させるために250

\* 位を有する下記一般式(1)で表わされるシロキサンポリイミドアミック酸共重合樹脂100重量部とエポキシ樹脂1～50重量部とを有機溶媒に溶解してなる電子材料用樹脂溶液組成物。

## 【化1】

※(2)で表わされ、シロキサンジアミンと芳香族ジアミンのモル比が、30/70～99/1である請求項1記載の電子材料用樹脂溶液組成物。

## 【化2】

℃以上の高温で長時間の硬化処理が必要となるため、硬化設備、作業性、生産性の点から問題があった。また、プリント基板等の保護膜にポリアミック酸ワニスを用いる場合には高温での熱処理によって銅箔回路表面に酸化膜が生じ、信頼性を低下させる原因にもなっていた。

【0003】一方、主鎖中にエーテル、スルホン、ケトンなどの化学構造を導入し、溶剤溶解性を改良した芳香族ポリアミック酸ワニスにおいても、有機溶剤中の樹脂濃度は塗布特性などにおける制限から最高でも20数%程度の樹脂濃度のものしか用いることができず、厚膜塗布が必要な用途の場合には、一度の処理によって十分な膜厚が得られないという問題があった。

【0004】かかる硬化温度や溶剤可溶性の問題を解決するための手法として、シロキサンジアミンを共重合によりポリマー主鎖中に導入したポリイミド、ポリアミック酸が提案され(特開昭57-143328号公報、特開昭58-13631号公報)、シロキサンジアミンの共重合比に応じて硬化温度と溶剤可溶性の改善が図られてはいるものの、逆に耐溶剤性が低下するという問題が生じた。

【0005】特に、シロキサンジアミン共重合比が高いシロキサンポリイミド樹脂は、N,N-ジメチルアセトアミド、N-メチル-2-ピロリドン等のアミド系溶剤、ジグライム等のグライム系溶剤はもちろんのこと、アセトン、メチルエチルケトン等の汎用のケトン系溶媒に対する耐溶剤性が低く、用途が限定されるという欠点を有していた。

【0006】更に、末端にアミノアルキル構造を有する汎用のシロキサンジアミンを用いたポリアミック酸ワニ

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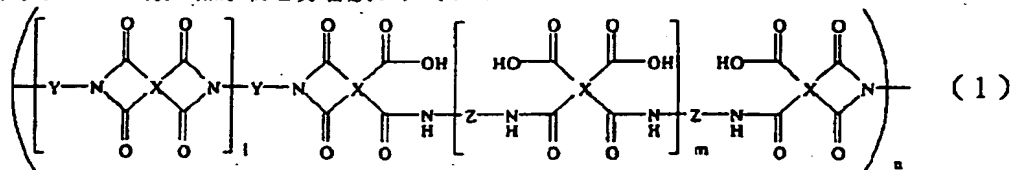
スは、ワニス中への水分の吸湿により容易に加水分解しやすく、保存中に粘度が低下するという問題点があった。

#### 【0007】

【発明が解決しようとする課題】したがって、本発明の目的は、保存安定性に優れ、比較的低温硬化が可能で、硬化後の耐熱性、高周波特性、耐薬品性、応力緩和特性などのバランスに優れた硬化物を与える電子材料用樹脂溶液組成物を提供することにある。

#### 【0008】

【課題を解決するための手段】本発明者らは、かかる課題について鋭意検討を重ねた結果、芳香族テトラカルボン酸二無水物とシロキサンジアミンからなるイミド部位及び芳香族テトラカルボン酸二無水物と芳香族ジアミン\*



(式中、Xは芳香族テトラカルボン酸二無水物残基を、Yはシロキサンジアミン残基を、Zは芳香族ジアミン残基を、l及びmはそれぞれ独立に整数を、nは1以上の数を示す)

【0010】以下、本発明を詳細に説明する。本発明において用いる芳香族テトラカルボン酸二無水物とは、カルボン酸基が芳香族に結合した化合物をいう。芳香族テトラカルボン酸二無水物の例を挙げると、ピロメリット酸二無水物、3,3',4,4'-ベンゾフェノンテトラカルボン酸二無水物、2,2',3,3'-ベンゾフェノンテトラカルボン酸二無水物、2,3,3',4'-ベンゾフェノンテトラカルボン酸二無水物、ナフタレン-2,3,6,7-テトラカルボン酸二無水物、ナフタレン-1,2,5,6-テトラカルボン酸二無水物、ナフタレン-1,2,4,5-テトラカルボン酸二無水物、ナフタレン-1,4,5,8-テトラカルボン酸二無水物、ナフタレン-1,2,6,7-テトラカルボン酸二無水物、2,6-ジクロロナフタレン-1,4,5,8-テトラカルボン酸二無水物、2,7-ジクロロナフタレン-1,4,5,8-テトラカルボン酸二無水物、2,3,6,7-テトラクロロナフタレン-1,4,5,8-テトラカルボン酸二無水物、1,4,5,8-テトラクロロナフタレン-2,3,6,7-テトラカルボン酸二無水物、3,3',4,4'-ジフェニルテトラカルボン酸二無水物、2,2',3,3'-ジフェニルテトラカルボン酸二無水物、2,3,3',4'-ジフェニルテトラカルボン酸二無水物、3,3'',4,4''-p-テルフェニルテトラカルボン酸二無水物、2,2'',3,3''-p-テルフェニルテトラカルボン酸二無水物、2,3,3'',4''-p-テルフェニルテトラカルボン酸二無水物、2,2-ビス(2,3-ジカルボキシフェニル)-プロパン二無水物、2,2-ビス(3,4-ジカルボキシフェニル)-プロパン二無水物、ビス(2,3-ジカルボキシフェニル)-エーテル二無水物、ビス(2,3

\*からなるアミック酸部位を有するポリイミドアミック酸共重合樹脂とエポキシ樹脂とを、有機溶媒に均一に溶解してなる樹脂溶液組成物が、前記課題を達成しうることを見出し、本発明を完成するに至った。

【0009】すなわち、本発明は、芳香族テトラカルボン酸二無水物とシロキサンジアミンを重縮合させてなるイミド部位及び芳香族テトラカルボン酸二無水物とシロキサンジアミン以外の芳香族ジアミン成分を重付加させてなるアミック酸部位を有する下記一般式(1)で表わされるシロキサンポリイミドアミック酸共重合樹脂100重量部とエポキシ樹脂1~50重量部とを有機溶媒に溶解してなる電子材料用樹脂溶液組成物である。

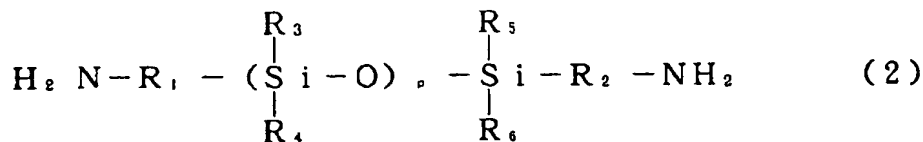
#### 【化3】

-ジカルボキシフェニル)メタン二無水物、ビス(3,4-ジカルボキシフェニル)メタン二無水物、ビス(2,3-ジカルボキシフェニル)スルホン二無水物、ビス(3,4-ジカルボキシフェニル)スルホン二無水物、1,1-ビス(2,3-ジカルボキシフェニル)エタン二無水物、1,1-ビス(3,4-ジカルボキシフェニル)エタン二無水物、ペリレン-2,3,8,9-テトラカルボン酸二無水物、ペリレン-3,4,9,10-テトラカルボン酸二無水物、ペリレン-4,5,10,11-テトラカルボン酸二無水物、ペリレン-5,6,11,12-テトラカルボン酸二無水物、フェナンスレン-1,2,7,8-テトラカルボン酸二無水物、フェナンスレン-1,2,6,7-テトラカルボン酸二無水物、フェナンスレン-1,2,9,10-テトラカルボン酸二無水物、ピラジン-2,3,5,6-テトラカルボン酸二無水物、チオフェン-2,3,4,5-テトラカルボン酸二無水物、4,4'-オキシジフタル酸二無水物などが挙げられる。これらは単独で使用してもよく、また2種以上を併用してもよい。これらのうち、特にビス(3,4-ジカルボキシフェニル)スルホン二無水物が、前記シロキサンポリイミドアミック酸共重合樹脂の有機溶媒に対する溶解性、銅面との密着性に優れているので好適である。

【0011】また、本発明において、芳香族テトラカルボン酸二無水物と共に使用するジアミン成分は、シロキサンポリイミドアミック酸共重合樹脂中のイミド部位を形成させるにはシロキサンジアミンを用い、ポリイミドアミック酸共重合樹脂中のアミック酸部位を形成させるには芳香族ジアミンを用いる。

【0012】本発明において用いるシロキサンジアミンは、下記一般式(2)で表されるものであることが好ましい。

【化4】



(式中、 $\text{R}_1$  及び  $\text{R}_2$  は二価の炭化水素基を、 $\text{R}_3 \sim \text{R}_6$  はそれぞれ炭素数1～6の炭化水素基を、 $p$  は1～30の整数を示す)

【0013】上記一般式(2)において、 $\text{R}_1$  及び  $\text{R}_2$  はそれぞれ炭素数3～5の複数のメチレン基又はフェニレン基、 $\text{R}_3 \sim \text{R}_6$  はメチル基、エチル基、プロピル基又はフェニル基、平均繰返し単位( $p$ )は1～20の整数であることが好ましい。

【0014】シロキサンジアミンの具体的化合物としては、例えば  $\omega$ ,  $\omega'$ -ビス(2-アミノエチル)ポリジメチルシロキサン、 $\omega$ ,  $\omega'$ -ビス(3-アミノプロピル)ポリジメチルシロキサン、 $\omega$ ,  $\omega'$ -ビス(4-アミノフェニル)ポリジメチルシロキサン、 $\omega$ ,  $\omega'$ -ビス(3-アミノプロピル)ポリジフェニルシロキサン、 $\omega$ ,  $\omega'$ -ビス(3-アミノプロピル)ポリメチルフェニルシロキサンなどが挙げられる。

【0015】本発明においては、シロキサンポリイミドアミック酸共重合樹脂の芳香族テトラカルボン酸二無水物とシロキサンジアミンが付加して形成されるイミド部位は、実質的に安定なイミドを形成していることが好ましい。

【0016】本発明で用いる芳香族ジアミンとは、アミノ基が芳香族に結合している化合物をいう。芳香族ジアミン例を挙げると、3,3'-ジメチル-4,4'-ジアミノビフェニル、4,6-ジメチル- $m$ -フェニレンジアミン、2,5-ジメチル- $p$ -フェニレンジアミン、2,4-ジアミノメシチレン、4,4'-メチレン-ジ- $o$ -トルイジン、4,4'-メチレン-ジ-2,6-キシリジン、2,4-トルエンジアミン、 $m$ -フェニレンジアミン、 $p$ -フェニレンジアミン、4,4'-ジアミノ-ジフェニルプロパン、3,3'-ジアミノ-ジフェニルプロパン、4,4'-ジアミノ-ジフェニルエタン、3,3'-ジアミノ-ジフェニルエタン、4,4'-ジアミノ-ジフェニルメタン、3,3'-ジアミノ-ジフェニルメタン、2,2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン、4,4'-ジアミノ-ジフェニルスルフィド、3,3'-ジアミノ-ジフェニルスルフィド、4,4'-ジアミノ-ジフェニルスルホン、3,3'-ジアミノ-ジフェニルスルホン、4,4'-ジアミノ-ジフェニルエーテル、3,3'-ジアミノ-ジフェニルエーテル、ベンジジン、3,3'-ジアミノ-ビフェニル、3,3'-ジメチル-4,4'-ジアミノ-ビフェニル、3,3'-ジメトキシ-ベンジジン、4,4'-ジアミノ- $p$ -テルフェニル、3,3'-ジアミノ- $p$ -テルフェニル、1,5-ジアミノ-ナフタレン、2,6-ジアミノ-ナフタレン、2,4-ジアミノ-トルエン、 $m$ -キシレン-2,5-ジア

ミン、 $p$ -キシレン-2,5-ジアミン、1,3-ビス(3-アミノフェノキシ)ベンゼンなどが挙げられる。これらは単独で使用してもよく、また2種以上を併用してもよい。これらのうち、特に2,2-ビス[4-(4-アミノフェノキシ)フェニル]プロパンが、前記シロキサンポリイミドアミック酸共重合樹脂の有機溶媒に対する溶解性などに優れているので好適である。

【0017】本発明において、通常重縮合系ポリマーの場合と同様にモノマー成分のモル比を調節することにより分子量を制御することができる。具体的には、全芳香族テトラカルボン酸二無水物1モルに対し、0.8～1.2モルのジアミンを使用することが好ましい。このモル比が0.8より小さかったり、1.2より大きくなると低分子量のものしか得られず、十分な耐熱性が得られない。更に好ましくは、芳香族テトラカルボン酸二無水物1モルに対し、0.95～1.05、最も好ましくは0.98～1.02モル比のジアミンの使用である。

【0018】本発明において、シロキサンジアミンと芳香族ジアミンのモル比は、30/70～99/1であることが好ましい。このモル比が30/70より小さいとシロキサンポリイミドアミック酸共重合樹脂の溶剤可溶性や硬化樹脂の応力緩和特性が悪化し、99/1を超えるとシロキサンポリイミドアミック酸共重合樹脂のエポキシ樹脂との反応点が少なくなり、硬化樹脂の耐薬品性が低下する。

【0019】本発明において用いるシロキサンポリイミドアミック酸共重合樹脂は、その分子量を目安として、対数粘度が0.08～1.2であることが好ましい。対数粘度は、シロキサンポリイミドアミック酸共重合樹脂をメチルジグリムに均一に溶解し、濃度0.5g/100mlの溶液を調製し、ウベローデ型粘度計によりその溶液粘度及びメチルジグリムの粘度を30℃で測定し、下記式で算出したものである。

対数粘度 =  $\ln(\text{溶液粘度} / \text{溶媒粘度}) / \text{溶液濃度}$   
シロキサンポリイミドアミック酸共重合樹脂の対数粘度が0.08より低いと硬化樹脂の耐薬品性、耐熱性が悪化し、1.2を超えると樹脂溶液組成物の粘度が高くなりすぎて作業性が低下する。

【0020】本発明において、シロキサンポリイミドアミック酸共重合樹脂と配合するエポキシ樹脂は、特に限定されるものではないが、エポキシ当量が100～5000特に100～1000程度である液状又は粉末状のエポキシ樹脂が好ましい。エポキシ樹脂の具体例としては、ビスフェノールA、ビスフェノールF、ビスフェノ



ールS、フルオレンビスフェノール、4,4'-ビフェノール、2,2'-ビフェノール、ヒドロキノン、レゾルシン等のフェノール類、トリス-(4-ヒドロキシフェニル)エタン、フェノールノボラック、o-クレゾールノボラック等の3価以上のフェノール類、又はテトラブロモビスフェノールA、ブロモフェノールノボラック等のハロゲン化ビスフェノール類から誘導されるグリシジルエーテル化合物などが挙げられる。これらは単独で使用してもよいし、2種以上を併用してもよい。樹脂溶液組成物の安定性のため、また低弾性率で応力緩和特性を有する硬化物を得るためには、エポキシ当量が比較的大きい2官能型のビスフェノール型エポキシ樹脂が好ましい。

【0021】エポキシ樹脂の配合量は、シロキサンポリイミドポリアミック酸共重合樹脂100重量部に対し、1〜50重量部であることを要し、好ましくは3〜30重量部である。エポキシ樹脂の配合量が、50重量部を超えると硬化樹脂の応力緩和特性や耐熱性などが低下し、また1重量部より少ないと耐薬品性が悪化する。

【0022】また、本発明においては、必要に応じて上記シロキサンポリイミドポリアミック酸共重合樹脂及びエポキシ樹脂の他に、硬化促進の目的でエポキシ樹脂硬化剤を配合することもできる。

【0023】本発明において用いられる有機溶媒は特に限定されるものではないが、本樹脂組成物を均一溶解可能なものならば、単独でもよいし、2種以上を併用した混合溶媒であっても差し支えない。例えば、フェノール系溶媒や、ピロリドン系溶媒、アセトアミド系溶媒等のアミド系溶媒や、ジオキサン、トリオキサン等のオキサン系溶媒や、シクロヘキサノン等のケトン系溶媒や、メチルジグリム、メチルトリグリム等のグリム系溶媒などが挙げられる。また必要に応じて、ベンゼン、トルエン等の芳香族炭化水素系溶媒やヘキサン、デカン等の脂肪族炭化水素系溶媒などを均一に溶解できる範囲で混合し使用することもできる。有機溶媒の量は、シロキサンポリイミドポリアミック酸共重合樹脂とエポキシ樹脂の合計量を固形分量としたとき、固形分と溶媒の重量比

(固形分/溶媒)が(20〜80)/(80〜20)であり、好ましくは(40〜70)/(60〜30)である。溶媒比が80を超えると十分な厚さの硬化物を得ることが難しくなり、溶媒比が20より少ないと樹脂溶液組成物の粘度が高くなりすぎて作業性が低下する。

【0024】

【発明の実施の形態】本発明の樹脂溶液組成物は、以下の方法で調製することができる。まず、予めシロキサンジアミンに対して過剰量の芳香族テトラカルボン酸二無水物を有機溶媒中に溶解又は懸濁させておき、シロキサンジアミンを徐々に添加する。混合物は室温付近の温度で2〜3時間攪拌した後、イミド化が進行しうる温度で縮合水を除去しながら10〜24時間重合とイミド化を行い、末端に酸無水物を有するシロキサンポリイミドオリ

ゴマーを得る。シロキサンポリイミドオリゴマーのイミド化率(%)は、赤外線吸収スペクトル分析法で測定して、実質的に100%であり、アミック酸部位がないことが好ましい。続いて、室温付近まで反応混合物を冷却後、酸無水物と全ジアミン成分が略等モル量になるように芳香族ジアミンを添加し、イミド化の進行しない温度で反応させてシロキサンポリイミドポリアミック酸共重合樹脂溶液を得る。次いで、ポリイミドポリアミック酸共重合樹脂溶液にエポキシ樹脂を均一に溶解させることにより、本発明の樹脂溶液組成物を得る。

【0025】ここで、反応に使用される有機溶媒は特に限定されるものではなく、前記の有機極性溶媒を使用することでもよいが、反応時間の短縮、溶媒散逸の問題により、沸点150℃以上のものがよく、特に200℃以上である有機極性溶媒(例えばメチルトリグリムなど)が最も好ましい。

【0026】本発明の樹脂溶液組成物には、上記各成分の他に、必要に応じて従来より公知の硬化促進剤、カップリング剤、充填剤、顔料、チクソトロピー性付与剤、消泡剤などを適宜配合してもよい。

【0027】

【実施例】以下、実施例により本発明を詳細に説明する。なお、樹脂溶液組成物の特性評価は下記の事項及び評価方法により行った。

【0028】〔はんだ耐熱性〕厚さ18μmの銅箔(三井金属株式会社製0.5オンス圧延箔)の銅粗化面に、熱処理後の膜厚が15〜20μmになるように各組成に調製した樹脂溶液組成物を流延して、130℃で15分間予備乾燥後、180℃で30分間熱処理し塗膜を作成する。1cm×2cmの塗付箔を作製し、300℃に調整した溶融はんだ浴に60秒間浸漬し、皮膜の銅表面からの剥離や皮膜外観上に変化の無いものを○とし、剥離や皮膜外観上に変化が生じたものを×として、はんだ耐熱性を評価した。

【0029】〔弾性率〕厚さ35μmの銅箔(三井金属株式会社製、1オンス圧延箔)に、熱処理後の膜厚が15〜20μmになるように各組成に調製した樹脂溶液組成物を流延して、130℃で15分予備乾燥後、180℃で30分間熱処理し塗膜を作製する。塗膜形成された銅箔はエッチング液により完全に銅を除去した後、12.5cm×20cmの皮膜試験片を作製し、引っ張り試験機(東洋精機株式会社製、STROGRAPH-R1)に取り付け、荷重100kg、引っ張り速度5mm/minで弾性率を測定した。

【0030】〔対数粘度〕シロキサンポリイミドポリアミック酸共重合樹脂の分子量の目安としての対数粘度は、シロキサンポリイミドポリアミック酸共重合樹脂をメチルジグリムに均一に溶解し、濃度0.5g/100mlの溶液を調製し、ウペローデ型粘度計によりその溶液粘度及びメチルジグリムの粘度を30℃で測定し、下記式で算出した。  
対数粘度 =  $\ln(\text{溶液粘度} / \text{溶媒粘度}) / \text{溶液濃度}$

【0031】〔溶液粘度〕各組成に調製した樹脂溶液組

成物の粘度はB型粘度計により25℃で測定した。

【0032】[アセトン可溶分]厚さ35 $\mu$ mの銅箔(三井金属株式会社製、1オンス圧延箔)に、熱処理後の膜厚が15~20 $\mu$ mになるように各組成に調製した樹脂溶液組成物を流延して、130℃で15分予備乾燥後、180℃で30分熱処理し塗膜を作製した。塗膜形成された銅箔はエッチング液により完全に銅を除去した後、10cm×10cmの皮膜を作製し、25℃のアセトン溶液に30分間浸漬し、皮膜の重量減少量をアセトン可溶分とした。

【0033】[誘電率]厚さ35 $\mu$ mの銅箔(三井金属株式会社製、1オンス圧延箔)の銅粗化面に、熱処理後の膜厚が40~50 $\mu$ mになるように各組成に調製した樹脂溶液組成物を流延し、130℃で15分予備乾燥後、180℃で30分熱処理して塗膜を作製した。作製した塗膜上に、上記同一種の銅箔の銅粗化面を、温度200℃、圧力40Kg/cm<sup>2</sup>で1時間熱圧着して両面銅張積層板を作製した。次いで、IPC-TM650.2.5.5A規格に従って両面銅張積層板を回路加工して誘電率測定用試験片を作製し、インピーダンスアナライザーに取り付け、1Mhzの誘電率を測定した。

#### 【0034】製造例1

攪拌器、窒素導入管を備えたDean-Shyurark型の反応器に、ビス(3,4-ジカルボキシフェニル)スルホン二無水物39.6g(0.110mol)とトリグリム118gを装入し、窒素雰囲気下で $\omega$ ,  $\omega'$ -ビス(3-アミノプロピル)ポリジメチルシロキサン71.4g(p=8, 0.093mol)を滴下ロートを用いて滴下し、室温で約2時間攪拌した。続いて、この反応溶液を窒素雰囲気下190℃に加熱して、水を除去しながら15時間加熱攪拌した。次いで、この反応溶液を室温まで冷却し、2,2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン7.1g(0.017mol)を加え、窒素雰囲気下に室温で攪拌しながら、この反応溶液を室温で約5時間攪拌し、固形分濃度51重量部のシロキサンポリイミドアミク酸共重合樹脂溶液を得た。得られたシロキサンポリイミドアミク酸共重合樹脂の対数粘度(温度30℃、濃度0.5g/100ml)は0.26であった。

#### 【0035】製造例2

攪拌器、窒素導入管を備えたDean-Shyurark型の反応器に、ビス(3,4-ジカルボキシフェニル)スルホン二無水物39.6g(0.110mol)とトリグリム120gを装入し、窒素雰囲気下で $\omega$ ,  $\omega'$ -ビス(3-アミノプロピル)ポリジメチルシロキサン76.3g(p=8, 0.099mol)を滴下ロートを用いて滴下し、室温で約2時間攪拌した。続いて、この反応溶液を窒素雰囲気下において190℃に加熱して、水を除去しながら15時間加熱攪拌した。次いで、この反応溶液を室温まで冷却し、2,2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン4.5g(0.011mol)を加え、窒素雰囲気下に室温で攪拌しながら、この反応溶液を室温で約5時間攪拌し、固形分濃度51重量部のシロキサンポリイミドアミク酸共重合樹脂溶液を得た。得られたシロ

キサンポリイミドアミク酸共重合樹脂の対数粘度(温度30℃、濃度0.5g/100ml)は0.23であった。

#### 【0036】製造例3

攪拌器、窒素導入管を備えた反応器に、ビス(3,4-ジカルボキシフェニル)スルホン二無水物39.6g(0.110mol)とトリグリム118gを装入し、窒素雰囲気下で $\omega$ ,  $\omega'$ -ビス(3-アミノプロピル)ポリジメチルシロキサン71.4g(p=8, 0.093mol)を滴下ロートを用いて滴下し、室温で約5時間攪拌した。次いで、この反応溶液に2,2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン7.1g(0.017mol)を加え、窒素雰囲気下に室温で攪拌しながら、この反応溶液を室温で約5時間攪拌し、固形分濃度50重量部のシロキサンポリイミドアミク酸共重合樹脂溶液を得た。得られたシロキサンポリイミドアミク酸共重合樹脂の対数粘度(温度30℃、濃度0.5g/100ml)は0.27であった。

#### 【0037】実施例1

500mlの反応器に、製造例1で得たシロキサンポリイミドアミク酸共重合樹脂溶液100gとビスフェノールA型エポキシ樹脂(東都化成株式会社製、YD-011、エポキシ当量=476)4.1gを装入し、室温で均一になるまで攪拌混合し、樹脂溶液組成物を得た。この樹脂溶液組成物を用いて、保存安定性試験、弾性率測定、はんだ耐熱試験、耐薬品性試験及び誘電率測定を行った。この樹脂溶液組成物は1週間室温で放置しても、均一な溶液の状態、粘度を保持していた。また、5℃以下の状態で3カ月間放置しても、粘度変化はほとんど観察されなかった。

#### 【0038】実施例2

500mlの反応器に、製造例1で得たシロキサンポリイミドアミク酸共重合樹脂溶液100gとビスフェノールA型エポキシ樹脂(東都化成株式会社製、YD-014、エポキシ当量=956)8.2gを装入し、室温で均一になるまで攪拌混合し、樹脂溶液組成物を得た。この樹脂溶液組成物を用いて、保存安定性試験、弾性率測定、はんだ耐熱試験、耐薬品性試験及び誘電率測定を行った。この樹脂溶液組成物は1週間室温で放置しても、均一な溶液の状態、粘度を保持していた。また、5℃以下の状態で3カ月間放置しても、粘度変化はほとんど観察されなかった。

#### 【0039】実施例3

500mlの反応器に、製造例2で得たシロキサンポリイミドアミク酸共重合樹脂溶液100gとビスフェノールA型エポキシ樹脂(東都化成株式会社製、YD-011、エポキシ当量=476)4.1gを装入し、室温で均一になるまで攪拌混合し、樹脂溶液組成物を得た。この樹脂溶液組成物を用いて、保存安定性試験、弾性率測定、はんだ耐熱試験、耐薬品性試験及び誘電率測定を行った。この樹脂溶液組成物は1週間室温で放置しても、均一な溶液の状態、粘度を保持していた。また、5℃以下の状態で3カ月間放置しても、粘度変化はほとんど観察されなかった。

#### 【0040】比較例1

エポキシ樹脂を用いなかったこと以外は実施例1と同様

に行い、保存安定性試験、弾性率測定、はんだ耐熱試験、耐薬品性試験及び誘電率測定を行った。その結果、この樹脂溶液組成物は耐薬品性が極めて悪く、アセトンにはほぼ完全に溶解した。

#### 【0041】比較例2

500mlの反応器に、製造例3で得たシロキサンポリアミック酸共重合樹脂溶液100gとビスフェノールA型エポキシ樹脂（東都化成株式会社製、YD-011、エポキシ当量=476）4.1gを装入し、室温で均一になるまで攪拌混合し、樹脂溶液組成物を得た。この樹脂溶液組成物を用いて、保存安定性試験、弾性率測定、はんだ耐熱試験、耐薬品性試験及び誘電率測定を行った。この樹脂溶液組成物は室温で1週間放置したところ、著しい粘度低下を示し \*

\*た。また、5℃以下の状態でも著しい粘度低下が観察された。

【0042】上記の実施例及び比較例の樹脂溶液組成物の配合組成並びに保存安定性試験、弾性率測定、はんだ耐熱試験、耐薬品性試験、誘電率測定の結果を表1に掲げる。ここで、弾性率測定、耐薬品性試験及び誘電率測定は、樹脂溶液組成物を製造した日[0day]に、溶液粘度測定及びはんだ耐熱性は、樹脂溶液組成物を製造した日[0day]と、90日間5℃の状態での保存した後[90day]に測定を行った。

#### 【0043】

【表1】

		実施例1	実施例2	実施例3	比較例1	比較例2
組成部	共重合樹脂溶液	100	100	100	100	100
	YD-011	4.1	0	4.1	0	4.1
	YD-014	0	8.2	0	0	0
	Bren-S	0	0	0	0	0
溶液粘度 [0day] (poise)		134	272	96	110	162
溶液粘度 [90day] (poise)		141	272	100	108	40
はんだ耐熱 [0day]		○	○	○	○	○
はんだ耐熱 [90day]		○	○	○	○	×
弾性率 (kgf/mm <sup>2</sup> )		38	37	19	27	37
アセトン可溶分 (wt%)		4	5	6	溶解	3
誘電率		3.2	3.2	3.2	3.2	3.2

#### 【0044】

【発明の効果】本発明の電子材料用樹脂溶液組成物は、保存安定性に優れ、180℃以下の低温硬化が可能であり、これを硬化すると耐熱性、高周波特性、耐薬品性、応力緩和特性等に優れた硬化物が得られる。したがって、

本発明の電子材料用樹脂溶液組成物は、例えばプリント基板等配線部品の層間絶縁膜や表面保護膜、あるいは半導体パッケージ用ダイボンディング剤、液状封止剤、その他電子材料用耐熱接着剤などに好適に使用することができる。

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